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(54) Title: EPOXIDATION CATALYST AND PROCESS (57) Abstract A catalyst comprising a porous refractory support having deposited thereon a catalytically effective amount of silver, a promoting amount of alkali metal, a promoting amount of rhenium, and a promoting amount of Group IVB metal applied to the support in the form of oxo compound(s). The catalyst is preparable by impregnating the support with solubilized silver and promoters, followed by calcination. The catalyst is intended for the epoxidation of olefins having no allylic hydrogen, in particular ethylene.		

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EPOXIDATION CATALYST AND PROCESS

This invention relates to supported silver-based catalysts suitable for the epoxidation of olefins having no allylic hydrogen, in particular ethylene and to the preparation and use of these catalysts.

5 Supported silver catalysts have long been used in the conversion of ethylene and oxygen to ethylene oxide. The use of small amounts of the alkali metals, K, Rb and Cs, were noted as useful promoters in supported silver catalysts in U.S. Pat. No. 3,962,136, issued June 8, 1976 and U.S. Pat. No. 4,010,115, issued
10 March 1, 1977.

 Rhenium was noted as being effective in improving selectivity of alkali metal doped silver based catalyst supported on a porous refractory support in U.S. Pat. No. 4,761,394 issued August 2, 1988 and in U.S. Pat. No. 4,833,261 issued May 23, 1989. U.S. Pat. No.
15 4,766,105 issued August 23, 1988, U.S. Pat. No. 4,820,675 issued April 11, 1989, and U.S. Pat. No. 4,808,738 issued February 28, 1989 further disclose the use of sulphur, Mo, W, Cr as rhenium co-promotor for such rhenium promoted catalyst.

 These rhenium promoted catalysts exhibit exceptionally high
20 selectivity as compared to conventional rhenium free catalysts. However, there is room for improvement as to their initial activity and activity decline rate.

 In commercial operation, reactor temperature is gradually increased to maintain an acceptable ethylene oxide production rate
25 as catalyst activity diminishes. Ethylene oxide catalysts are generally run until the upper temperature limit of the unit is reached. Also, acceptable selectivity must be maintained throughout the life of the catalyst. The lifespan of a catalyst depends on five factors: 1) initial activity, 2) activity decline rate, 3)
30 upper temperature limit of the reactor, 4) initial selectivity, and 5) selectivity decline rate.

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Increasing initial catalytic activity as well as holding activity and selectivity stability for rhenium promoted catalyst, while maintaining the selectivity advantage, is believed to be one of the most critical issues for the development of an improved high selectivity rhenium promoted catalyst with long catalyst life.

Some references in the art have suggested the use of group IVB metals as an ingredient in the silver based ethylene oxide catalyst. U.S. Pat. No. 4,908,343 issued March 13, 1990 and U.S. Pat. No. 5,057,481 issued October 15, 1991 disclosed cesium promoted, silver based supported catalysts containing oxyanion of group 3b through group 7b, including, among a large group of oxyanions, titanate and zirconate.

European patent application 266,015 published May 4, 1988 disclosed a silver based ethylene oxide catalyst containing rhenium metal promoter and at least one further metal promoters. A large number of metals, including group IVB metals, were listed as suitable further metal promoters. The metal promoters are believed to be present as oxidic compounds in numerous forms listed, including oxides, hydroxides, nitrates, sulphates, carboxylates, carbonates, bicarbonates, oxyhalides, etc,. However, there was no mention as to which oxidic form provides better catalytic performance.

It has now been found, that the addition of group IVB oxo salts to a silver based ethylene oxide catalyst, having a promoting amount of alkali metal and promoting amount of rhenium, provides substantial improvement in both initial activity and long term stability in selectivity, while the high initial selectivity advantage of prior art rhenium promoted catalysts is maintained. Furthermore, the activity advantage is maintained throughout the catalyst life time.

This invention relates to a catalyst comprising a porous refractory support having deposited thereon a catalytically effective amount of silver, a promoting amount of alkali metal, a promoting amount of rhenium, and a promoting amount of Group IVB metal applied to the support in the form of oxo compound(s).

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Other promoters in promoting amounts may be optionally present in the catalyst, such as rare earths, magnesium, rhenium co-promoters selected from sulphur, chromium, molybdenum, tungsten and mixture thereof.

5 In broad general term, the catalysts of the instant invention are prepared by impregnating porous refractory supports with silver ions or compound(s), complex(es) and/or salt(s) dissolved in a suitable solvent sufficient to cause deposition on the support of a promoting amount of silver; the thus impregnated carrier is then
10 separated from the solution and the deposited silver compound is reduced to metallic silver. Also deposited on the support either prior to, coincidentally with, or subsequent to the deposition of the silver will be a promoting amount of suitable ions, or compound(s) and/or salts(s) of alkali metal dissolved in a suitable
15 solvent, promoting amount of suitable rhenium ion(s) or compound(s), complex(es) and/or salt(s) dissolved in an appropriate solvent, and promoting amount of group IVB metal(s) provided in the form of oxo complexes or compound(s) and/or salt(s) thereof dissolved in a suitable solvent.

20 The preferred method is to deposit silver, rhenium metal, alkali metal and Group IVB metal oxo complex promoters simultaneously on the support, that is, in a single impregnation step, although it is believed that the individual or concurrent deposition of the alkali metal and Group IVB metal oxo complex,
25 prior to and/or subsequent to the deposition of the silver would also produce suitable catalysts.

The support or carrier employed in the catalysts of the present invention in its broadest aspect is selected from the larger number of conventional, porous refractory catalyst carriers or support
30 materials which are considered relatively inert in the presence of the ethylene oxidation feeds, products and reaction conditions. Such conventional materials are known to those skilled in the art and may be of natural or synthetic origin and preferably are of a macroporous structure, i.e., a structure having a surface area
35 ranging from 0.05 to 10 m²/g and preferably below 3 m²/g.

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Particularly suitable supports are those of aluminous composition, in particular those comprising alpha alumina. In the case of alpha alumina-containing supports, preference is given to those having a specific surface area as measured by the B.E.T. method of from 0.03 to 10, preferably from 0.05 to 5, more preferably from 0.1 to 3 m²/g, and a water pore volume as measured by conventional water absorption techniques of from 0.1 to 0.75, preferably from 0.3 to 0.5 ml/g. The B.E.T. method for determining specific surface area is described in detail in Brunauer, S., Emmet, P. Y. and Teller, E., J. Am. Chem. Soc., 60, 309-16 (1938). Suitable alpha alumina-containing supports are particularly described in U.S. Pat. No. 4,761,394. Suitable manufacturers of carriers include Norton Company and United Catalysts, Inc. (UCI).

A particularly preferred support suitable for use in the present invention comprises alpha alumina based carrier having a crush strength of at least 2.5 kg and a settled packing density of at least 0.48 kg/l foot which comprises a first alpha alumina component in the form of particles having a median crystallite size of from 0.4 to 4 µm providing from 95% to 40% of the total weight of alpha alumina in the carrier and a second alpha alumina component generated in situ by a sol-gel process and providing the balance of the alpha alumina in the carrier. In a still more particularly preferred support, it further comprises from 0.05% to 1% by weight of titania, based on the weight of alumina in the carrier.

The support is preferably shaped into particles, chunks, pieces, pellets, rings, spheres, wagon wheels, and the like of a size suitable for use in fixed bed reactors. Conventional commercial fixed bed reactors are typically in the form of a plurality of parallel elongated tubes (in a suitable shell) approximately 12 to 64 mm I.D. and 4.5-14 m long filled with catalyst particles in rounded shape having diameters from 1 mm to 20 mm.

Promoting amounts of group IVB metal, provided in the form of oxo complex(es), or mixtures thereof are deposited on a porous support using a suitable solution prior to, coincidentally with, or

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subsequent to the deposition of the silver and/or alkali metal and/or rhenium. As used herein, the term "Group IVB metal" and cognates thereof refers to the Group IVB metals, according to the CAS version of the Periodic Table, selected from the group consisting of titanium, zirconium and hafnium and mixtures thereof. As a preferred embodiment of the present invention, promoting amounts of hafnium oxo compound(s) or zirconium oxo compound(s), or mixtures thereof are first dissolved in a suitable solution prior to being deposited on the carrier. As a particularly preferred embodiment, promoting amounts of hafnium oxo compound(s) are used. Without intending to limit the scope of the invention, an oxo compound of Group IVB metals comprises an "oxo" moiety which is a Group IVB metal atom/ion doubly bonded to oxygen atom. This "oxo moiety" can be covalently or ionically bound to other atoms/ions such as chloride, carbonate, nitrate, etc. Examples of suitable compounds of Group IVB metal oxo compound(s) include oxyhalide, oxycarbonate, oxynitrate of hafnium and/or zirconium, i.e. HfOCl_2 , HfOCO_3 , $\text{HfO}(\text{NO}_3)_2$, ZrOCl_2 , ZrOCO_3 , $\text{ZrO}(\text{NO}_3)_2$, etc. Optionally, the Group IVB oxo compound(s) can be further complexed or coordinated with other ligands or complexing agents such as amine containing ligands. As a preferred embodiment of the present invention, the Group IVB oxo compound(s) are dissolved in an aqueous solution containing ammonium carbonate before being deposited on the support.

It is believed that ammonium carbonate facilitates in solubilizing the Group IVB oxo-containing compounds in the aqueous solution.

The amount of Group IVB metal deposited upon the support generally lies between 0.01 and 10, preferably between 0.05 and 5 and most preferably between 0.1 and 2 micromoles per gram of the total catalyst.

After being deposited on the catalyst carrier, the group IVB metal promoters, which were initially added to the impregnation solution as oxo complexes, may present on the catalysts in the form of oxo complexes, cations (ions) or compounds of complexes or surface compounds or surface complexes rather than as the free Group

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IVB metallic elements, although for convenience purposes in this specification and claims they are referred to as "Group IVB metal" or "Group IVB metal promoters".

Promoting amounts of alkali metal or mixtures of alkali metal are deposited on the porous support using a suitable solution. Although alkali metals exist in a pure metallic state, they are not suitable for use in that form. They are used as ions or compounds of alkali metals dissolved in a suitable solvent for impregnation purposes.

The amount of alkali metal promoter deposited upon the support or present on the catalyst generally lies between 10 and 3000, preferably between 15 and 2000, more preferably between 20 and 1500 and most preferably, the amount ranges between 50 and 1000 parts per million by weight of the total catalyst.

The alkali metal promoters are present on the catalysts in the form of cations (ions) or compounds of complexes or surface compounds or surface complexes rather than as the extremely active free alkali metals, although for convenience purposes in this specification and claims they are referred to as "alkali metal" or "alkali metal promoters". It is believed that the alkali metal compounds are oxidic compounds. More particularly, it is believed that the alkali metal compounds are probably in the form of mixed surface oxides or double surface oxides or complex surface oxides with the aluminium of the support and/or the silver of the catalyst, possibly in combination with species contained in or formed from the reaction mixture, such as, for example, chlorides or carbonates or residual species from the impregnating solution(s).

In a preferred embodiment, at least a major proportion (greater than 50%) of the alkali metals are selected from the group consisting of lithium, potassium, cesium, and mixtures thereof.

A preferred alkali metal promoter is cesium. A particularly preferred alkali metal promoter is cesium plus at least one additional alkali metal, which is preferably selected from sodium, lithium and mixtures thereof, with lithium being preferred.

It should be understood that the amounts of alkali metal or

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Group IVB metal promoters on the catalysts are not necessarily the total amounts of these metals present in the catalyst. Rather, they are the amounts of alkali metal or Group IVB promoters which have been added to the catalyst by impregnation. These amounts do not include amounts of alkali metals or Group IVB metals which are locked into the support, for example, by calcining, or are not extractable in a suitable solvent such as water or lower alkanol or amine or mixtures thereof and do not provide a promoting effect. It is also understood that a source of the alkali metal or Group IVB metal promoter ions, complexes, salts and/or compounds used to promote the catalyst may be the carrier. That is, the carrier may contain extractable amounts of alkali metal or Group IVB metal that can be extracted with a suitable solvent, such as water or lower alkanol, thus preparing an impregnating solution from which the alkali metal or Group IVB metal ions, complexes, salts and/or compounds are deposited or redeposited on the support.

Other promoters and co-promoters can be used in conjunction with the silver, rhenium promoters, alkali metal promoters and Group IVB metal promoters. Non-limiting examples of other promoters include molybdate, sulfate, tungstate and chromate (see U.S. Pat. No. 4,766,105, issued August 23, 1988); fluoride anion, oxyanions of Groups 3b to 6b (see U.S. Pat. No. 5,102,848, issued April 7, 1992); (i) oxyanions of an element selected from Groups 3 through 7b and (ii) alkali(ne) metal salts with anions of halides, and oxyanions selected from Groups 3a to 7a and 3b through 7b (see U.S. Pat. No. 4,908,343, issued March 13, 1990). It is noted that sulfate anion when deposited in the amount of 1 to 2 micromoles per gram of total catalyst prepared by depositing thereon 1-2 micromoles of rhenium, 5.0 micrograms of lithium, 0.5-1.0 micromoles of hafnium oxyhalide and 500 to 700 micromoles of cesium per gram of the total catalyst does not necessarily enhance the activity or selectivity of the present catalyst. However, it is believed that sulfate anion present in different amounts, or when combined with other promoters or copromoters and/or when combined promoters or copromoters in different amounts might still be beneficial.

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The carrier is also impregnated with rhenium ions, salt(s), compound(s) and/or complex(es) prior to, coincidentally with, or subsequent to the deposition of the silver and/or alkali metal and/or Group IV metal. The amount of rhenium promoter preferably present on the catalyst generally lies between 0.1 to 10, more preferably between 0.2 to 5 micromoles (basis metal) per gram of total catalyst.

Suitable rhenium promoters, the form of the rhenium metal on the catalyst, the promoting effects, etc. are described in U.S. Pat. No. 4,761,394.

Generally, the carrier is contacted with a silver salt, a silver compound, or a silver complex which has been dissolved in an aqueous solution, so that the carrier is impregnated with said aqueous solution; thereafter the impregnated carrier is separated from the aqueous solution, e.g., by centrifugation or filtration and then dried. The thus obtained impregnated carrier is heated to reduce the silver to metallic silver. It is conveniently heated to a temperature in the range of from about 50°C to about 600°C, during a period sufficient to cause reduction of the silver salt, compound or complex to metallic silver and to form a layer of finely divided silver, which is bound to the surface of the carrier, both the exterior and pore surface. Air, or other oxidizing gas, reducing gas such as hydrogen containing gas, an inert gas or mixtures thereof may be conducted over the carrier during this heating step. As a specific embodiment of the present invention, the reduction is conducted in the presence of air. As another specific embodiment of the present invention, the said reduction is conducted by contacting the impregnated carrier with a gas comprising hydrogen, or an inert gas containing at least about 4 volume percent hydrogen. As still another specific embodiment of the present invention, the impregnated carrier is first subjected to a calcination procedure wherein a gas, such as air, oxygen-depleted air, inert gases such as nitrogen, argon, helium, etc. or any mixture thereof, is passed over or through the impregnated carrier at a temperature of about 250 to 350°C. for about 2-4 hours, and then subject to reduction under a

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gas comprising at least 4 volume percent hydrogen.

One method of preparing the silver containing catalyst can be found in U.S. Pat. No. 3,702,259. Other methods for preparing the silver-containing catalysts which in addition contain higher alkali metal promoters can be found in U.S. Pat. No. 4,010,115, U.S. Pat. No. 4,356,312, U.S. Pat. No. 3,962,136 and U.S. Pat. No. 4,012,425. Methods for preparing silver-containing catalysts containing higher alkali metal and rhenium promoters can be found in U.S. Pat. No. 4,761,394 and methods for silver-containing catalysts containing higher alkali metal and rhenium promoters and a rhenium co-promoters can be found in U.S. Pat. No. 4,766,105. Methods for preparing silver-containing catalysts with a variety of different promoters are found in U.S. Pat. No. 4,908,343 and U.S. Pat. No. 5,057,481.

A particularly preferred process of impregnating the catalyst consists of impregnating the carrier with an aqueous solution containing a silver salt of a carboxylic acid, an organic amine, a salt of cesium, a salt of hafnium oxychloride, and a salt of rhenium dissolved therein. Silver oxalate is a preferred silver salt. It can be prepared by reacting silver oxide (slurry in water) with (a) a mixture of ethylenediamine and oxalic acid, or (b) oxalic acid and then ethylenediamine, which latter is preferred, so that an aqueous solution of silver oxalate-ethylenediamine complex is obtained, to which solution is added a certain amount of cesium compound, rhenium compound and hafnium oxo salt. While addition of the amine to the silver oxide before adding the oxalic acid is possible, it is not preferred since it can give rise to solutions which are unstable or even explosive in nature. Other diamines and other amines, such as ethanolamine, may be added as well. The impregnated carriers are then heated to a temperature between about 50°C and about 600°C, preferably between about 75°C and about 400°C to evaporate the liquid and produce a metallic silver.

The concentration of the silver (expressed as the metal) in the silver-containing solution will range from 1 g/l up to the solubility limit when a single impregnation is utilized. The concentration of the alkali metal (expressed as the metal) will

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range from 1×10^{-3} to 12 and preferably, from 10×10^{-3} to 12 g/l when a single impregnation step is utilized. The concentration of the rhenium will range from 8×10^{-2} to 8 g/l. The concentration of the group IVB metal will range from 5×10^{-2} to 5 g/l.

5 Concentrations selected within the above noted ranges will depend upon the pore volume of the catalyst, the final amount desired in the final catalyst and whether the impregnation is single or multiple. Appropriate concentrations can be readily determined by routine experimentation.

10 It is observed that independent of the form in which the silver is present in the solution before precipitation on the carrier, the term "reduction to metallic silver" is used, while in the meantime often decomposition by heating occurs. We prefer to use the term "reduction", since Ag^+ ion is converted into a metallic Ag atom.

15 Reduction times may generally vary from 0.5 minute to 8 hours, depending on the circumstances. The amount of silver deposited on the support or present on the support is to be a catalytically effective amount of silver, i.e., an amount that provides a measurable conversion of ethylene and oxygen to ethylene oxide.
20 Preferably this amount will range from 1 to 30, more preferably from 1 to 25, and even more preferably from 5 to 20 percent by weight of the total catalyst.

In commercial operations, ethylene and oxygen are converted to ethylene oxide in a reactor which comprises a large fixed tube sheet
25 heat exchanger containing several thousand tubes filled with catalyst. A coolant is used on the shell side of the reactor to remove the heat of reaction. Coolant temperatures are frequently utilized as an indication of catalyst activity, high coolant temperatures corresponding to lower catalyst activities. In the
30 vapour phase reaction, the ethylene is present in at least a double amount (on a mole basis) compared with oxygen, but is often much higher. Therefore the conversion is calculated according to the molar percentage of oxygen which has been used in the reaction. The oxygen conversion is dependent on the reaction temperature which
35 latter is a measure of the activity of the catalyst employed. The

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value T_{40} indicates the temperature at 40 mole percent conversion of the oxygen in the reactor and the value T is expressed in °C. This temperature is generally higher when the conversion of oxygen is higher. Moreover, this temperature is strongly dependent on the employed catalyst and the reaction conditions. The selectivity (to ethylene oxide) indicates the molar amount of ethylene oxide in the reaction product compared with the total molar amount ethylene converted. Herein the selectivity is indicated as S_{40} , which means the selectivity at 40 molar percent oxygen conversion. The selectivity of silver based ethylene oxide catalysts can decrease over a period of time of usage. When comparing the selectivity performance of various silver-based ethylene oxide catalysts, it is important that the selectivity value be measured at approximately the same period of time of usage under the same or similar reaction conditions. As used herein, "initial selectivity" will refer to the selectivity of ethylene oxide catalysts when measured at a given constant oxygen conversion level of 40% at a gas hourly space velocity of approximately 3300 and when measured after the catalyst has been placed on stream for about 16 ± 4 hours. Unless otherwise noted, all selectivities that are provided in the examples provided herein are initial selectivities. Alternatively, severity can be expressed as the level of EO production. For example, $T_{1.5}$ is defined as the temperature required to produce an outlet EO level of 1.5%. $S_{1.5}$ is defined as the selectivities at 1.5% EO production.

The conditions for carrying out an ethylene oxidation reaction in the presence of the silver catalysts according to the present invention broadly comprise those already described in the prior art. This applies, for example, to suitable temperatures, pressures, residence times, diluent materials, such as nitrogen, carbon dioxide, steam, argon, methane or other saturated hydrocarbons, presence of moderating agents to control the catalytic action, for example, 1,2-dichloroethane, vinyl chloride, ethyl chloride or chlorinated polyphenyl compounds, the desirability of employing recycle operations or applying successive conversions in different reactors to increase the yields of ethylene oxide, and any other

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special conditions which may be selected in processes for preparing ethylene oxide. Pressures in the range of from atmospheric to 35 bar are generally employed. Higher pressures are, however, by no means excluded. Molecular oxygen employed as reactant can be obtained from conventional sources. The suitable oxygen charge may consist essentially of relatively pure oxygen, a concentrated oxygen stream comprising oxygen in major amount with lesser amounts of one or more diluents, such as nitrogen and argon, or another oxygen-containing stream, such as air. It is therefore evident that the use of the present silver catalysts in ethylene oxidation reactions is in no way limited to the use of specific conditions among those which are known to be effective. For purposes of illustration only, the following table shows the range of conditions that are often used in current commercial ethylene oxide reactor units and which are also suitable for the instant process.

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TABLE I

*GHSV	1550 - 10,000
Inlet pressure	1000 - 3800 kPa
<u>Inlet Feed</u>	
ethylene	10 - 40%
O ₂	3 - 12%
CO ₂	0.1 - 40%
ethane	0 - 3%
Argon and/or methane and/or nitrogen diluent	
chlorohydrocarbon moderator	0.3 - 20 ppmv total
Coolant temperature	180 - 315 °C
Catalyst temperature	180 - 325 °C
O ₂ conversion level	10 - 60%
EO Production (Work Rate)	32 - 320 kg EO/m ³ catalyst/hr.

* Volume units of gas at standard temperature and pressure passing over one volume unit of packed catalyst per hour.

In a preferred application of the silver catalysts according to the present invention, ethylene oxide is produced when an oxygen-containing gas is contacted with ethylene in the presence of the present catalysts at a temperature in the range of from 180°C to 330°C and preferably from 200°C to 325°C.

While the catalysts of the present invention are preferably used to convert ethylene to ethylene oxide, they can be also used to epoxidise other olefins having no allylic hydrogens, such as are broadly defined in U.S. Patent No. 4,897,498 issued January 30, 1990. Exemplary of such olefins are butadiene, tertiary butyl ethylene, vinyl furan, methyl vinyl ketone, N-vinyl pyrrolidone, and the like. A presently preferred olefin for use in the practice of this process is butadiene, because of its ready availability, relative low cost, and the wide range of possible uses for the epoxide reaction product. U.S. Patent No. 5,081,096, issued January 14, 1992, discloses a silver-based, alkali metal-promoted, supported

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catalyst which is adapted to the epoxidation of butadiene by treating the pro-catalyst, after its impregnation with a silver compound and promoters and following calcination, with a hydrogen containing gas at temperature not exceeding 350 °C. The same can be done with the catalysts according to the present invention.

Prior to use for oxidizing olefins having no allylic hydrogens, the silver catalysts (either before or after further treatment with promoter), are optionally calcined in an oxygen-containing atmosphere (air or oxygen-supplemented helium) at about 350°C for about 4 hours. Following calcination, the silver catalysts are typically subjected to an activation treatment at a temperature in the range of 300°-350°C in an atmosphere initially containing 2-5% hydrogen in an inert carrier such as helium or nitrogen. The hydrogen content of the activating atmosphere is gradually increased up to a final hydrogen concentration of about 20-25% at a controlled rate so that the activation temperature does not exceed 350°C. After the temperature is maintained for about 1 hour at a hydrogen concentration in the range of about 20-25%, catalyst is ready for use.

ILLUSTRATIVE EMBODIMENTS

ILLUSTRATIVE EMBODIMENT I:

The following illustrative embodiment describes typical preparative techniques for making the catalysts of the instant invention (and comparative catalysts) and the typical technique for measuring the properties of these catalysts.

Catalysts A-1, A-2, A-3: Experimental Catalysts Promoted by Hf Oxo Compounds

Part A: Preparation of stock silver oxalate/ethylenediamine solution for use in catalyst preparation:

1. Dissolve 415 g reagent-grade NaOH in 2340 deionized water. Adjust temperature to 50°C.
2. Dissolve 1699 g "spectropure" (high-purity) AgNO₃ in 2100 ml deionized water. Adjust temperature to 50°C.
3. Add NaOH solution slowly to AgNO₃ solution with stirring, maintaining temperature at 50°C. Stir for 15 minutes after addition

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is complete, then lower temperature to 40°C. Measure the pH, which should be greater than 10.

5 4. Insert clean filter wands and withdraw as much water as possible from the precipitate created in step (3) in order to remove sodium and nitrate ions. Measure the conductivity of the water removed and add back as much fresh deionized water as was removed by the filter wands. Stir for 15 minutes at 40°C. Repeat this process until the conductivity of the water removed is less than 90 micro-mho/cm. Then add back 1500 ml deionized water.

10 5. Add 630 g of high-purity oxalic acid dihydrate in approximately 100g increments. Keep the temperature at 40°C. and stir to mix thoroughly. Add the last portion of oxalic acid dihydrate slowly and monitor the pH to ensure that the pH does not drop below 7.8. Aim for a pH endpoint of 8.0-8.4. Add high-purity silver oxide if
15 necessary to achieve this endpoint.

6. Remove as much water as possible with clean filter wands. Cool the slurry of silver oxalate to 30°C. Record the weight of the slurry.

20 7. Add 699 g of 92% ethylenediamine (8% deionized water). Do not allow the temperature to exceed 30°C. during addition.

The above procedure yields a solution containing approximately 27-33%w silver which provides the "stock solution" used in the preparation of Catalysts A-1,2,3, B-1,2,3, C-1,2,3,4, and the standard below.

25 Part B: Preparation of Impregnation Solutions

For catalyst A-1:

1. Dissolve 0.160 g NH_4ReO_4 and 0.138 g LiNO_3 in 3.0 ml of deionized water.
2. Dissolve 0.164 g $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ (hafnium oxychloride octahydrate)
30 in 2.0 ml saturated aqueous $(\text{NH}_4)_2\text{CO}_3$ solution.
3. Dissolve 0.058 g CsOH in 0.19 ml H_2O .
4. With stirring, add the solutions from step 1, 2 and 3, and 20.3 g of deionized water to 178.7 grams of stock silver solution from Part A to make total weight of 204 grams of impregnation solution.
- 35 5. One-fourth of this solution is used for the carrier

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5 impregnation to prepare the catalyst A-1. As shown in Table III, Catalyst A-1 using this impregnation solution following the impregnation and curing procedures in Part C below will yield catalysts which contain approximately 13.5%w Ag by weight of the total catalyst, 1.5 micromoles of rhenium, 5.0 micromoles of lithium, 380 ppm of cesium, and 1.0 micromoles of hafnium, expressed as the metal, by weight of the total catalyst. The catalysts are approximately optimum in cesium for the given silver and rhenium levels and support with regard to initial selectivity under the test conditions described below.

10 For Catalysts A-2 and A-3: The procedure for Catalyst A-1 is followed, except that different amounts of Hf and Cs are added to the impregnation solutions which were calculated to result in different levels of Hf and Cs loadings as shown in Table III.

15 Part C: Catalyst Impregnation and Curing

A catalyst carrier having the properties described below was used in Catalysts A-1, A-2 and A-3:

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TABLE II
Properties of Carrier

Alpha Alumina	(Balance)
Nitric Acid Leachables in ppm	
Na	50-150
K	65 Max
Ca	800-1000
Aluminium	450-600
SiO ₂	1300-1700
Leachables in ppm	
Na (Water Test)	42.9
Na (Acetic Acid Test)	89.3
K (Water Test)	23.7
K (Acetic Acid Test)	52.7
Water absorption	61.1%
Crush Strength,	11.3
> 5.4 kg	98%
< 4.1 kg	1.0%
**Surface Area,	0.48 m ² /g
*Total Pore Volume	0.421

* Measured by Micromeritics 9310 Poresizer

** Measured on Micromeritics 2600 Surface Area Analyzer

5 The carrier was impregnated as follows: Approximately 30 grams of the carrier was placed under 25 mm vacuum for 3 minutes at room temperature. Approximately 50 g of the impregnating solution from Part B above was then introduced to submerge the carrier, and the vacuum was maintained at 25 mm for an additional 3 minutes. At the end of this time, the vacuum was released, and the excess impregnating solution was removed from the carrier by centrifugation for 2 minutes at 500 rpm. The impregnated carrier was then cured by being continuously shaken in a 8500 liter/hr air stream at 250°C for 10 5 minutes. The cured catalysts were ready for testing.

TABLE III

Compositions of the Catalysts						
* micromoles/gram of catalyst						
** parts per million by weight of total catalyst						
Catalyst	Group IVB	Re *	Li *	Cs **	Hf *	Zr *
A-1	HfOCl ₂	1.5	5.0	380	1.0	0.0
A-2	HfOCl ₂	1.5	5.0	420	0.6	0.0
A-3	HfOCl ₂	1.5	5.0	420	0.3	0.0
B-1	ZrOCl ₂	1.5	5.0	340	0.0	0.5
B-2	ZrOCl ₂	1.5	5.0	340	0.0	0.5
B-3	ZrO(NO ₃) ₂	1.5	5.0	380	0.0	0.5
C-1	HfSO ₄	1.5	8.0	540	0.55	0.0
C-2	HfSO ₄	1.2	8.0	540	0.55	0.0
C-3	Zr(NO ₃) ₄	1.5	8.0	440	0.0	0.5
C-4	(NH ₄) ₂ ZrF ₆	1.5	8.0	420	0.0	0.5
Standard		1.5	5.0	350-550	0.0	0.0

The actual silver content of the catalyst can be determined by any of a number of standard, published procedures. The actual level of rhenium on the catalysts prepared by the above process can be determined by extraction with 20 mM aqueous sodium hydroxide solution, followed by spectrophotometric determination of the rhenium in the extract. The actual level of hafnium on the catalyst by the above process can be determined by total acid digestion followed by inductively coupled plasma jet analysis (Direct Current Plasma Atomic Emission Technique). The actual level of zirconium on the catalyst by the above process can be determined by total acid digestion followed by inductively coupled plasma jet analysis (Direct Current Plasma Atomic Emission Technique). The actual level

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of cesium on the catalyst can be determined by employing a stock cesium hydroxide solution, which has been labelled with a radioactive isotope of cesium, in catalyst preparation. The cesium content of the catalyst can then be determined by measuring the radioactivity of the catalyst. Alternatively, the cesium content of the catalyst can be determined by leaching the catalyst with boiling deionized water. In this extraction process cesium, as well as the other alkali metals, it is measured by extraction from the catalyst by boiling 10 grams of whole catalyst in 25 millilitres of water for 5 minutes, repeating the above two more times, combining the above extractions and determining the amount of alkali metal present by comparison to standard solutions of reference alkali metals using atomic absorption spectroscopy (using Varian Techtron Model 1200 or equivalent).

Part D: Standard Microreactor Catalyst Test
Conditions/Procedures

The following describes the microreactor catalyst test conditions and procedures used in Illustrative Embodiment 1 to test the catalysts for the production of ethylene oxide from ethylene and oxygen.

Three to five grams of crushed catalyst (1.4-0.84 mm, 14-20 mesh) are loaded into a 6.4 mm inch internal diameter stainless steel U-shaped tube. The U tube is immersed in a molten metal bath (heat medium) and the ends are connected to a gas flow system. The weight of catalyst used and the inlet gas flow rate are adjusted to achieve a gas hourly space velocity of 3300 ml of gas per ml of catalyst per hour. The inlet gas pressure is 1450 kPa.

The gas mixture passed through the catalyst bed (in once-through operation) during the entire test run (including start-up) consists of 30% ethylene, 8.5% oxygen, 5% CO₂, 0.5% argon, balance nitrogen, and 0.5 to 5 ppmv ethyl chloride.

Prior to being contacted with the reactant gases, the catalysts are typically pretreated with nitrogen gas at 225°C for 3 hours.

The initial reactor (heat medium) temperature is 225°C. After 1 hour at this initial temperature, the temperature is increased to

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235°C for 1 hour, followed by 245°C for 1 hour. The temperature is then adjusted so as to achieve a constant oxygen conversion level of 40% (T_{40}). The moderator level is varied and run for 4-24 hours at each moderator level to determine the optimum moderator level for maximum selectivity. Performance data at the optimum moderator level and at T_{40} are usually obtained when the catalyst has been onstream for a total of at least 36 hours and are provided in the illustrative embodiments given below. Due to slight differences in feed gas composition, gas flow rates, and the calibration of analytical instruments used to determine the feed and product gas compositions, the measured selectivity and activity of a given catalyst may vary slightly from one test run to the next. To allow meaningful comparison of the performances of catalysts tested at different times, all catalysts described in this illustrative embodiment were tested simultaneously with a standard reference catalyst.

Catalysts B-1, B-2, B-3: Experimental Catalysts Promoted by Zr Oxo Compounds

Catalysts B-1, B-2 and B-3 were prepared following the same procedures as described above for Catalyst A-1 using a carrier with similar properties as that listed in Table II, except that zirconium oxo salts, $ZrOCl_2$ or $ZrO(NO_3)_2$ were used in lieu of $HfOCl_2$. The approximate levels of dopant loaded are shown in Table II.

Catalysts C-1, C-2, C-3 and C-4: Experimental Catalysts Promoted by Non-Oxo Hf or Zr Compounds

Catalysts C-1, C-2, C-3 and C-4 were prepared following the same procedures as described above in Illustrative Embodiment I using a carrier with similar properties as that listed in Table II, except that Group IVB metals are provided in non-oxo forms. $HfSO_4$ was used for Catalysts C-1 and C-2, $Zr(NO_3)_4$ was used for Catalyst C-3 and $(NH_4)_2ZrF_6$ was used for Catalyst C-4. The approximate dopant levels loaded were listed in Table II.

Standard Catalysts without Group IVB Metals

A large number of standard catalysts were prepared in a manner similar to Catalysts A-1,2,3 and B-1,2,3, except that no Group IVB

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compound is present in the impregnation solutions. The loadings of lithium, rhenium, and silver were the same as Catalysts A-1,2,3 and B-1,2,3. Catalysts with various cesium loadings, from 350 ppm to 550 ppm were prepared to obtain standard catalysts having optimum selectivities at T_{40} matching that of Catalysts A-1,2,3, B-1,2,3 and C-1,2,3. A large database of the performances of these standard catalysts was established. The compositions of the resulted standard catalysts is shown in Table III above.

Results

The catalysts above were tested using the above process, the results thereof are given in Table IV below. Activity data are expressed as the temperature at which the catalyst achieve 40% oxygen conversion of 40% (T_{40}). T_{40} of experimental catalysts are compared to corresponding T_{40} of the standard catalysts containing no Group IVB ingredient that performs at the same selectivity.

As shown from the results given in Table IV below, the experimental catalysts prepared from the impregnation solutions containing either hafnium oxo salts (Catalysts A-1, A-2, and A-3) or zirconium oxo salts (Catalysts B-1, B-2, B-3) exhibit substantial improvement in initial activities as illustrated by the lower T_{40} required to reach 40% conversion, as compared with the corresponding standard catalysts without group IVB ingredients. However, the experimental catalysts prepared from the impregnation solutions containing group IV metal ingredients in the non-oxo form (Catalysts C-1, C-2, C-3, and C-4) exhibit no improvement in initial activities.

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TABLE IV

Group IVB Containing Catalyst	Group IVB Compound	Group IVB Catalyst Performance		Standard Catalyst Activity At Same Selectivity T ₄₀ (°C)
		S ₄₀ (%)	T ₄₀ (°C)	
A-1	HfOCl ₂	84.5	241	254
A-2	HfOCl ₂	86.0	250	262
A-3	HfOCl ₂	85.7	247	261
B-1	ZrOCl ₂	85.0	248	258
B-2	ZrOCl ₂	84.8	249	258
B-3	ZrO(NO ₃) ₂	84.8	242	258
C-1	HfSO ₄	86.1	259	259
C-2	HfSO ₄	83.0	244	244
C-3	Zr(NO ₃) ₄	84.4	252	254
C-4	(NH ₄) ₂ ZrF ₆	84.1	256	253

ILLUSTRATIVE EMBODIMENT 2

Catalyst A-4 was prepared in the same manner and on the same carrier as Catalyst A-1 described in Illustrative Embodiment 1. The amounts of rhenium/lithium/hafnium oxychloride loaded on the carrier were 1.5/5.0/1.0 micromoles per gram of carrier. The cesium loading was 387 ppm.

The comparison catalyst SA-4 was prepared in the same manner as catalyst A-4 on the same carrier. Rhenium/lithium loadings were 1.5/5/0 micromoles per gram of carrier. No hafnium salt was loaded. The cesium loading was 480 ppm.

Catalysts A-4 and SA-4 were microreactor tested by the same process as described in Illustrative Embodiment 1 above, except that the test continued for 215 days. The results are shown in Table V below. The Hafnium oxyhalide impregnated catalyst A-4 exhibited an improved initial activity, improved final activity after 215 days, and improved final selectivity after 215 days, relative to the

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standard catalyst SA-4. (* The end-of-run selectivities (15 day averages) for SA-4 and A-4 (Hf) were 75.8% and 78.2%, respectively).

As mentioned previously, increasing catalytic activity as well as holding activity and selectivity stability to achieve longer catalyst life for rhenium promoted catalysts is of tremendous economic importance. The data suggest that the addition of hafnium oxo salts to the impregnation solution provides an improvement in both the initial catalytic activity and long-term performance.

TABLE V

Catalyst	HfOCl ₂ μm/g	Initial T ₄₀ °C	Final T ₄₀ °C	Initial S ₄₀ %	Final S ₄₀ %
Catalyst A-4	1.0	249	265	85.4	78.1
Comparative Catalyst SA-4	0	260	277	84.8	76.3

ILLUSTRATIVE EMBODIMENT 3

Catalyst A-5 was prepared in the same manner as Catalyst A-1 described in Illustrative Embodiment 1, except a carrier having the compositions and the properties listed in TABLE VI and TABLE VII for the preparation of the catalyst. The amounts of rhenium/lithium/hafnium oxychloride loaded on the carrier were 1.5/12.0/0.75 micromoles per gram of carrier. The cesium loading was 540 ppm.

The comparison catalyst SA-5 was prepared in the same manner as catalyst A-5 on the same carrier. Rhenium/lithium loadings were 1.5/12.0 micromoles per gram of carrier. No hafnium salt was loaded. The cesium loading was 580 ppm.

Catalyst A-6 was prepared in the same manner as Catalyst A-5 described above, except 1.5 micromole of sulfate per gram of carrier was loaded. The amounts of rhenium/lithium/ sulfate/hafnium oxychloride loaded on the carrier were 1.5/12.0/ 1.5/0.75 micromoles

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per gram of carrier. The cesium loading was 660 ppm.

The comparison catalyst SA-6 was prepared in the same manner as catalyst A-6 on the same carrier. Rhenium/lithium/ sulfate loadings were 1.5/12.0/1.5 micromoles per gram of carrier. No hafnium salt was loaded. The cesium loading was 680 ppm.

TABLE VI
CARRIER COMPOSITION

Alpha Alumina #1 ^{1,2}	46.6
Alpha Alumina #2 ^{1,3}	28.0
Alpha Alumina #3 ^{1,4}	None
Alpha Alumina #4 ^{1,5}	None
Alpha Alumina #5 (Seed) ^{1,6}	0.9
TiO ₂ ¹	0.2
ZrO ₂ ¹	None
Gibbsite ^{1,7}	18.7
Boehmite ^{1,8}	4.5
Ceramic Bond ^{1,9,11,12}	1.3
Organic Burnout ¹⁰	11.0
Petrolatum ¹⁰	5.0
Boric Acid ¹⁰	0.15
Water (to make extrudable) ¹³	~30

¹ Indicates "ceramic components" and percentages given are based on 100% of the ceramic components.

² "Alpha Alumina #1" is an alpha alumina that had a median particle size of about 3 to about 3.4 microns, a BET surface area of about 0.9 to about 1.4 m²/g, a crystallite size of about 1.6 to about 2.2 microns and a soda content of about 0.02% to about 0.06%.

³ "Alpha Alumina #2" is an alpha alumina with a median particle size of about 4.0 to about 8.0 microns, a surface area of about 3.0 to about 5.0 m²/g, a crystallite size of from about 0.4 to

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about 0.8 micron and a soda content of about 0.1% to about 0.3%.

4 "Alpha Alumina #3" is an alpha alumina that had a median
particle size of 3.6 to 4.2 microns, a BET surface area of
5 about 0.8 to about 1.0 m²/g, a crystallite size of 3 to 4
microns and a soda content of about 0.05%.

5 "Alpha Alumina #4" is an alpha alumina that had a median
particle size of 2.5 to 3.5 microns, a BET surface area of
about 3 to about 4 m²/g, a crystallite size of 3 to 4 microns
10 and a soda content of about 0.1%.

6 "Alpha Alumina #3" is an alpha alumina that was used as the
seed for the gibbsite and boehmite precursors of alpha alumina.
Its median particle size was less than 0.1 micron.

7 The gibbsite had a median particle size of from about 4.0 to
15 about 20 microns.

8 The boehmite was dispersible as a sol.

9 The ceramic bond for carriers A and B contained components,
expressed as the oxides, in the following approximate
proportions: 60% wt. silica, 29% wt. alumina, 3% wt. calcium
20 oxide, 2% magnesia, 4% wt. alkali metal oxides and less than 1%
wt. each of ferric oxide and titania.

10 Percentages are based on the total weight of the ceramic
components.

11 The ceramic bond for Carrier C contained components, expressed
as oxides, in the following approximate proportions: 67% wt.
25 silica, 30% wt. alumina, about 1% wt. each of ferric oxide and
titania, and a trace of alkali metal and alkaline earth oxides.

12 The ceramic bond used for Carrier D was calcium silicate.

13 Percentages are based on total weight of solids.

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TABLE VII
CARRIER PROPERTIES

Water Absorption, % ¹	38.3
Packing Density, lbs/ft ³ ²	50.9
Crush Strength, lbs ³	14.9
Surface Area, m ² /g ⁴	1.01
Acid Leachables, ppm	
Na	350
K	76
Ca	149
Al	579
TiO ₂ , %	0.2
Firing Temperature, °C	1450

- 1 "Water Absorption" is a measure of the increase in weight of the carrier after being immersed in water and weighed.
- 2 "Packing Density" is the settled packing density as measured by ASTM D-4699-87, modified by the use of cylinder with an inside diameter of 95.25 mm and a length of 457 mm, or an equivalent.
- 3 "Crush Strength" is measured on a Compton Tensile Tester, model 50-OP.
- 4 "Surface Area" is the BET surface area measured using nitrogen or krypton as the adsorbate.

10 Catalysts A-5 and SA-5 were microreactor tested by the following process:

Three to five grams of crushed catalyst (1.4-0.84 mm, 14-20 mesh) were loaded into a 5.8 mm internal diameter stainless steel U-shaped tube. The U tube was immersed in a molten metal bath (heat medium) and the ends were connected to a gas flow system. The weight of catalyst used and the inlet gas flow rate were adjusted to achieve a gas hourly space velocity of 6800 ml of gas per ml of catalyst per hour. The inlet gas pressure was 1450 kPa. The gas mixture passed through the catalyst bed (in once-through operation) during the entire test run (including start-up) consists of 25%

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ethylene, 7.0% oxygen, 5% CO₂, 0.5% argon, balance nitrogen, and 0.5 to 5 ppmv ethyl chloride. Prior to being contacted with the reactant gases, the catalysts were pretreated with nitrogen gas at 225°C for 3 hours.

5 The initial reactor (heat medium) temperature was 225°C. After
1 hour at this initial temperature, the temperature was increased to
235°C for 1 hour, followed by 245°C for 1 hour. The temperature was
then adjusted so as to achieve a constant ethylene oxide production
level of 1.5% (T_{1.5}). The moderator level was varied and run for 4-
10 24 hours at each moderator level to determine the optimum moderator
level for maximum selectivity. Performance data at the optimum
moderator level and at T_{1.5} were obtained when the catalyst had been
onstream for a total of at least 36 hours and are provided in TABLE
VIII given below.

TABLE VIII

Catalyst	Re/SO ₄ /Li μm/g	HfOCl ₂ μm/g	S _{1.5} %	T _{1.5} °C
Catalyst A-5	1.5/0/12	0.75	86.3	242
Comparative Catalyst SA-5	1.5/0/12	0	85.0	246
Catalyst A-6	1.5/1.5/12	0.75	86.1	242
Comparative Catalyst SA-6	1.5/1.5/12	0	88.9	258

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C L A I M S

1. A catalyst comprising a porous refractory support having deposited thereon a catalytically effective amount of silver, a promoting amount of alkali metal, a promoting amount of rhenium, and a promoting amount of Group IVB metal applied to the support in the form of oxo compound(s).
2. The catalyst of claim 1, characterized in that the Group IVB metal is selected from the group consisting of zirconium and hafnium.
3. The catalyst according to claim 1 or 2, wherein the support comprises at least 85 percent by weight of alpha alumina, having a water pore volume from 0.1 to 0.75 ml/g, and having a surface area from 0.03 to 10 m²/g, and the catalyst contains (expressed as metal per gram total catalyst) 1-30 wt% of silver, 0.01-10 μmol of Group IV metal, 3000 parts per million of alkali metal and 0.1-10 μmol of rhenium.
4. The catalyst of claim 3, wherein said support has a crush strength of at least 2.57 kg and a settled packing density of at least 0.48 kg/litre and which support comprises a first alpha alumina component in the form of particles having a median crystallite size of from 0.4 to 4 μ providing from 95% to 40% of the total weight of alpha alumina in the carrier and a second alpha alumina component generated in situ by a sol-gel process and providing the balance of the alpha alumina in the carrier.
5. The catalyst of claim 5 wherein said support further comprises from 0.05% to 1% by weight of titania, based on the weight of alumina in the carrier.
6. The catalyst of any one of claims 1-5, wherein said Group IVB metal oxo compound applied to the support is selected from the group consisting of the metal oxyhalide, oxynitrate or oxycarbonate.
7. The catalyst of any one of claims 1-6, wherein said alkali metal promoter comprises cesium.

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8. The catalyst of claim 7, wherein said alkali metal promoter comprises cesium plus at least one additional alkali metal.

9. The catalyst of any one of claims 1-8, which further comprises a rhenium co-promoter selected from sulphur, molybdenum, tungsten, chromium and mixtures thereof.

10. A process for the preparation of the catalyst of claim 1, comprising impregnating a porous, refractory support with
(a) a solubilized catalytically effective amount of silver,
(b) a solubilized promoting amount of alkali metal,
(c) a solubilized promoting amount of rhenium metal, and
(d) a solubilized promoting amount of a Group IVB metal oxo compound and, optionally after impregnation, reducing the silver to metallic silver.

11. The process of claim 10, wherein the impregnated support is intimately contacted, over a temperature range of 170°C to 600°C, with a gas comprising at least 4 volume percent of hydrogen.

12. A process for the production of ethylene oxide comprising the steps of contacting ethylene in the vapour phase with an oxygen-containing gas at ethylene oxide forming conditions at a temperature ranging between 180°C and 330°C in the presence of a catalyst according to any one of claims 1-9.

13. A process for the epoxidation of olefins having no allylic hydrogen comprising the steps of contacting the olefins in the vapour phase with an oxygen-containing gas maintain at a ratio of olefin to oxygen in the range of 0.01 to 20, at epoxide forming conditions at a temperature in the range of from 75°C to 330°C in the presence of a halogen or halide, and a catalyst according to any one of claims 1-9, which catalyst after the impregnation of the metals, has been put in intimate contact with a gas containing at least 4 volume percent of hydrogen.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/EP 94/04341

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B01J 23/68, C07D 301/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B01J, C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EDOC, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A1, 0266015 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.), 4 May 1988 (04.05.88), page 2, line 32 - line 35; page 3, line 37 - line 42; page 6, line 1 - page 7, line 5, page 8, line 46 - line 54; page 11, line 6 - page 12, line 17, claims 1,2,5,9,12,13,16,18,20,23,27, abstract --	1-13
A	US, A, 5187140 (ERLIND M. THORSTEINSON ET AL), 16 February 1993 (16.02.93), column 11, line 8 - column 13, line 36; column 16, line 46 - line 50; column 17, line 21 - line 27, column 35, line 10 - line 11, claims 1,21,26,31,33, abstract --	1-13

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/EP 94/04341

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP, A1, 0326392 (EASTMAN KODAK COMPANY), 2 August 1989 (02.08.89), claims 1,4,5,10, abstract -----	5,13

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INTERNATIONAL SEARCH REPORT
Information on patent family members

09/02/95

International application No.

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			US-A-	4820675	11/04/89
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			US-A-	4833261	23/05/89
US-A-	5187140	16/02/93	AU-B-	639946	12/08/93
			AU-A-	5036793	13/01/94
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